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(54) Title of the Invention: Resin Composition for Mechanical Foam Coating

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SPECIFICATION

1. Title of the Invention

Resin Composition for Mechanical Foam Coating

2. Claims

- (1) A resin composition for mechanical foam coating comprising as principal components an aqueous medium, surfactant, and hydrophobic resin, characterized by being compounded with a higher aliphatic alcohol.
- (2) The resin composition according to Claim 1, wherein the higher aliphatic alcohol is a primary alcohol having 9 to 20 carbons.
- (3) The resin composition according to Claim 1, further compounded with a substantially unvulcanized natural rubber, modified natural rubber, or synthetic rubber.
- (4) The resin composition according to Claim 1 wherein the hydrophobic resin is a polyacrylic ester resin, polyurethane resin, or a mixture thereof.

3. Detailed Description of the Invention

The present invention relates to a resin composition for foam coating that is suitable when a foam coating layer is provided to a support comprising a woven fabric, nonwoven fabric, nap fabric, plastic sheet-paper, or the like.

Conventionally known methods for forming a foam layer on a support include those in which a variety of required additives is added to an aqueous resin composition formed by finely dispersing a synthetic resin or other hydrophobic polymer in water using a surfactant, mechanical foaming is induced, the foam is applied to a nap fabric or other support, and heat is used to cause the foam to gel (e.g., JP (Kokai) 47-35103, JP (Kokoku) 44-6718, and US Patent 3,804,700).

An extremely critical yet troublesome technical aspect with such prior art is that fine bubbles are produced when latex foam is formed, and in general these bubbles readily aggregate and have a pronounced tendency to form into large bubbles. It accordingly needs to be determined how these fine bubbles are to be preserved during the step where the foamed layer is applied to the support and heated to form into a gel. Preserving the fine and densely foamed state in such a manner will have a definitive impact on the value of the end product. An example of a method for resolving such drawbacks is disclosed in JP (Kokai) 47-35103, wherein sodium

lauryl sulfate is employed as a foaming agent, but the effect of preserving the bubbles in a fine and dense state is virtually non-existent despite the foaming agent being effective in producing foam. On the other hand, the use of ammonium stearate, ammonium biphenate, or another higher aliphatic ammonium salt is disclosed in US Patent 3,804,700. Such compounds have an exceptional effect in preserving the bubbles in a fine state, but when the foam has been applied to a support and dried, numerous cracks will appear in the resulting coating layer, and the ammonium salt used after heat-induced gelation will migrate in large amounts to the surface of the layer, thereby considerably degrading the value of the resulting end product.

The present inventors conducted diligent investigations into resolving the drawbacks of resin compositions for mechanical foam coating as has been described in the foregoing, and perfected the present invention based on the discovery that extremely fine and dense foam could be obtained when a specific substance had been added to a resin composition, such a state could be preserved for long periods of time, no cracks would appear from drying, and the additives would not migrate to the surface even after the end product has been fabricated, thereby enabling a highly exceptional foam coating to be formed.

In other words, the present invention is a resin composition for mechanical foam coating comprising as principal components an aqueous medium, surfactant, and hydrophobic resin, with the resin composition characterized by being compounded with a higher aliphatic alcohol.

A detailed description of the present invention shall now be provided. The resin composition used as a base in the present invention encompasses all conventional resin compositions for mechanical foam coatings employed in relevant technical fields; e.g., acrylic resins, urethane resins, vinyl acetate resins, vinyl chloride resins, styrene resins, vinyl propionate resins, styrene-butadiene resins, acrylonitrile-butadiene resins, acrylonitrile-butadiene-styrene resins, polyisoprene, chloroprene, and natural rubber as well as other latexes, and can encompass a variety of additives as required; e.g., surfactants, gelling promoters, dyestuffs/pigments, fillers, antioxidants, stabilizers, viscosity adjusters, curing agents, and gelling agents.

The higher aliphatic primary alcohol that is used in the present invention and is a distinctive feature of this invention is a straight or branched chain synthetic or natural alcohol; e.g., octanol, decanol, lauryl alcohol, myristyl alcohol, cetyl alcohol, 14-methylhexadecanol,

stearyl alcohol, 16-methyloctadecanol, eicosanol, and 18-methylnonadecanol. Equally, synthetic alcohols having an odd number of carbons may also be used. It was discovered that primary alcohols having 9 to 20 carbons, and especially 14 to 20 carbons, were the most effective among these alcohols. The alcohols are preferably used in an amount of approximately 3 to 10 weight parts per 100 weight parts of resin in the latex.

The essential components of the resin composition for mechanical foam coating of the present invention are essentially the prior-art resin compositions for mechanical foam coating and the aforementioned higher aliphatic alcohols. However, it was discovered that particularly when acrylic or urethane resin compositions are used, the effect of the present invention could be dramatically enhanced by adding as an ancillary additive approximately 5 to 20 wt% of substantially unvulcanized (i.e., not yet subjected to a vulcanization step) natural (as well as modified) rubber latexes, aqueous dispersions of synthetic rubbers (latexes), or a mixture thereof to the acrylic or urethane resins (solid fraction), in addition to the aforementioned essential components. Examples of such natural rubber latexes include natural rubber latex and modified natural rubber latexes (e.g., natural rubber latexes that have been graft-polymerized with acrylic acid ester), and examples of synthetic rubber latexes include aqueous dispersions of the aforementioned varieties of synthetic rubbers and their modified synthetic rubbers. It was discovered that the effect of the present invention was significantly more pronounced when these substances were added.

The resin composition of the present invention is manufactured by using any conventional method to admix the higher aliphatic alcohol that characterizes the present invention, either alone or with the aforementioned rubber latexes, into the aforementioned conventionally known resin composition; however, it is normally advantageous to adjust the solid fraction to approximately 30 to 70 wt% and the viscosity to between approximately 5,000 and 20,000 cps in the steps described hereunder.

The resin composition of the present invention obtained as described in the foregoing is stirred mechanically by means of a common method; e.g., by means of an Oakes mixer as the air is blown thereinto to trap air in the material and to form a cream-like foam at a foaming rate of approximately 170 to 400%. Next, the foamed product is applied in a thickness of approximately

0.5 to 10 mm onto various optionally pretreated supports, heated and dried at a temperature of approximately 100 to 170°C, and formed into a heated gel to yield a foam layer. The bubbles in the cream-like foam obtained by mechanical means are very dense and fine, and these fine bubbles can be kept stable for extremely long periods of time, as compared to those obtained in the prior art. Adopting this approach makes it possible to substantially resolve problems related increased bubble sizes during subsequent steps; i.e., when the foam is applied to the support, dried, and caused to gel. With conventional methods, moreover, large bubbles form, and numerous cracks appear in the coated layer when the layer is dried, which largely degrades the value of the product. However, when the resin composition of the present invention is used, the bubbles essentially do not become large as the steps are performed, and therefore the occurrence of cracking in the coated layer is entirely eliminated, resulting in a foam coating layer that has exceptional hand, is extremely dense and highly flexible, and contains individual cells and communicating pores. Foam coating layers obtained by means of conventional methods generally exhibit poor physical characteristics at low temperatures, but the resin composition of the present invention was found to exhibit dramatically improved physical characteristics at low temperatures as well.

The resin composition for foam coating of the present invention may be applied to any support, and the foam coating later may be formed in various thicknesses. For example, the composition is advantageously utilized in the manufacture of synthetic leather, a variety of leather-like articles, cushioning sheets, decorative paper, decorative boards, wallpaper, and the like. In particular, using the resulting foam coating layer as a breathable cushioning middle layer and applying various coatings or surface treatments on the layer is preferred for the manufacture of a variety of synthetic leather, artificial leather, and other similar sheet-like products that resemble natural leather.

The present invention is described in detail below with reference to working examples. All references to "parts" or "%" in the description relate to weight.

Working Example 1

The three resin compositions I to III below were prepared according to conventional methods. The foam stabilizer of the present invention and a conventional foam stabilizer were

added to these resin compositions to prepare the resin compositions for mechanical foam coating (A through C) in accordance with the present invention, and to prepare similar types of conventional resin compositions (a through j).

– Preparation of resin compositions (I to III)

Resin composition I

Polyacrylate ester emulsion (Rohm and Haas Co.; solid fraction: 50%):	100	parts
Crosslinking agent:	5	parts
Crosslinking catalyst:	0.5	parts
Thickener:	5	parts
Extender pigment (alumina):	10	parts

Resin composition II

Polyurethane emulsion (Bayer AG; solid fraction: 40%):	100	parts
Crosslinking agent:	5	parts
Crosslinking catalyst:	0.5	parts
Thickener:	5	parts
Extender pigment (alumina):	10	parts

Resin composition III

Polyacrylate ester emulsion (Rohm and Haas Co.; solid fraction: 50%):	50	parts
Polyurethane emulsion (Bayer AG; solid fraction: 40%):	50	parts
Crosslinking agent:	5	parts
Crosslinking catalyst:	0.5	parts
Thickener:	10	parts

– Preparation of resin compositions of the present invention (A to C)

Resin composition A: Mixture obtained by adding 5 parts of stearyl alcohol to 120.5 parts of resin composition I

Resin composition B: Mixture obtained by adding 5 parts of a synthetic primary aliphatic alcohol having 14 to 16 carbons and 10 parts of unvulcanized styrene-butadiene rubber latex (JSR Co., Ltd.; solid fraction: 60%) to 120.5 parts of resin composition II

Resin composition C: Mixture obtained by adding 5 parts of a synthetic primary aliphatic alcohol having 14 to 16 carbons and 10 parts of unvulcanized styrene-butadiene rubber latex (JSR Co., Ltd.; solid fraction: 60%) to 120.5 parts of resin composition III

- Preparation of conventional resin compositions (*a* to *f*; comparative resin composition)

Resin composition *a*: Mixture obtained by adding 5 parts of ammonium stearate to 120.5 parts of resin composition I

Resin composition *b*: Mixture obtained by adding 5 parts sodium of lauryl sulfate to 120.5 parts of resin composition I

Resin composition *c*: Mixture obtained by adding 5 parts of ammonium stearate to 120.5 parts of resin composition II

Resin composition *d*: Mixture obtained by adding 5 parts of sodium lauryl sulfate to 120.5 parts of resin composition II

Resin composition *e*: Mixture obtained by adding 5 parts of ammonium stearate to 120.5 parts of resin composition III

Resin composition *f*: Mixture obtained by adding 5 parts of sodium lauryl sulfate to 120.5 parts of resin composition III

Working Example 2

A formulation comprising 100 parts polyurethane elastomer solution (Rezamine ME; Dainichiseika Color & Chemicals Mfg. Co., Ltd.), 10 parts colorant (Seika Seven E color), and 20 parts solvent was applied to a release sheet and dried, resulting in 10 μ -thick films. The aforementioned resin compositions A to C and *a* to *f* were expanded to a foaming rate of 200% with the aid of a mechanical foaming mixer, and the resulting creamy foam was applied to the films in an amount that produced a thickness of 0.5 mm. A knitted base fabric was laminated under contact pressure on the coating layer at normal temperature, and the product was dried and caused to gel immediately thereafter for 10 min at 150°C, resulting in synthetic leather products. Evaluations were made of the bubbling state, product quality, and manner in which the foam stabilizer had migrated in the aforementioned steps. The results are shown in Table 1.

Table 1

Resin composition	Bubbling state (note 1a)	Bubbling state (note 1b)	Product quality (note 2)	Migration of foam stabilizer (note 3)
A	Excellent	Excellent	Excellent	Excellent
B	Excellent	Excellent	Excellent	Excellent
C	Excellent	Excellent	Excellent	Excellent
a	Excellent	Good	Fair	Poor
b	Poor	Poor	Poor	Excellent
c	Excellent	Good	Fair	Poor
d	Poor	Poor	Poor	Excellent
e	Excellent	Good	Fair	Poor
f	Poor	Poor	Poor	Excellent

Note 1(a) A comparison was made between the bubbling states observed immediately after the products had expanded 200% and 10 minutes after the products had been left to stand, to examine the amount of aggregated large bubbles. "Excellent": no change at all; "Good": a small proportion of large bubbles; "Poor": significant proportion of large bubbles.

Note 1(b) The compositions were applied to Rezamine films immediately after the products had expanded 200%, and the amount of aggregated large bubbles was examined after the resulting articles had been left to stand for one minute. The levels of assessment were the same as those indicated in aforementioned Note 1(a).

Note 2 "Excellent": Surface film and foam layer were formed as integrated whole, and no cracks formed in the foam layer. The bubbles were extremely dense and fine.
 "Fair": Surface film and foam layer were formed as integrated whole, but the bubbles were fairly large, and numerous cracks appeared.
 "Poor": Pronounced formation of large bubbles, and poor surface state.

Note 3 The surface state of the products was observed after they had been immersed for 24 hrs in tap water at normal temperature, removed, and dried.
 "Excellent": No evidence of the foam stabilizer migrating to the surface.
 "Poor": Pronounced migration

Working Example 3

The aforementioned resin compositions A to C and *a* to *f* were each expanded 200% with a mechanical foaming mixer, applied to a base fabric (Moss 4A) in a thickness of approximately 0.4 to 0.5 mm with a knife coater, and then heated and dried to form a gel at 150°C for 10 min to yield original fabrics having foam layers that were approximately 0.2 to 0.3 mm thick. Synthetic leather products were obtained by applying the same film-forming compositions as those used in Working Example 2 onto these original fabrics at a rate of approximately 100 g/cm² using a knife coater, drying the resulting articles, then applying a polyamino acid resin topcoating agent at a rate of approximately 70 g/m², and drying the resulting articles. When the resin composition of the present invention was used in the manufacture of such products, a very good and uniformly fine bubbling state was obtained, large bubble aggregations did not form during the steps, the surfaces of the resulting products had the fine wrinkles seen in natural leather patterns, the layers of the product were completely integrated with each other, and no cracks appeared in the foam layer. Moreover, the surfaces were stable when washed with water or dry-cleaned, and there was no incidence of the foam stabilizer migrating to the surface. On the other hand, when resin compositions *a*, *c* and *e* were used, the resulting products were similar to those obtained with the resin composition of the present invention, but fairly large bubbles appeared in the foam layers, a high incidence of cracking occurred, the foam stabilizer migrated to the surface after the products were dried following a washing test, and the product value was significantly degraded. When resin compositions *b*, *d* and *f* were used, large bubbles formed when the foam was applied, the surface became very rough when the middle and surface layers were formed, and virtually no product value was retained.

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SPECIFICATION

1. Title of the Invention

Resin Composition for Mechanical Foam Coating

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2. Claims

- (1) A resin composition for mechanical foam coating comprising as principal components an aqueous medium, surfactant, and hydrophobic resin, characterized by being compounded with a higher aliphatic alcohol.
- (2) The resin composition according to Claim 1, wherein the higher aliphatic alcohol is a primary alcohol having 9 to 20 carbons.
- (3) The resin composition according to Claim 1, further compounded with a substantially unvulcanized natural rubber, modified natural rubber, or synthetic rubber.
- (4) The resin composition according to Claim 1 wherein the hydrophobic resin is a polyacrylic ester resin, polyurethane resin, or a mixture thereof.

3. Detailed Description of the Invention

The present invention relates to a resin composition for foam coating that is suitable when a foam coating layer is provided to a support comprising a woven fabric, nonwoven fabric, nap fabric, plastic sheet-paper, or the like.

Conventionally known methods for forming a foam layer on a support include those in which a variety of required additives is added to an aqueous resin composition formed by finely dispersing a synthetic resin or other hydrophobic polymer in water using a surfactant, mechanical foaming is induced, the foam is applied to a nap fabric or other support, and heat is used to cause the foam to gel (e.g., JP (Kokai) 47-35103, JP (Kokoku) 44-6718, and US Patent 3,804,700).

An extremely critical yet troublesome technical aspect with such prior art is that fine bubbles are produced when latex foam is formed, and in general these bubbles readily aggregate and have a pronounced tendency to form into large bubbles. It accordingly needs to be determined how these fine bubbles are to be preserved during the step where the foamed layer is applied to the support and heated to form into a gel. Preserving the fine and densely foamed state in such a manner will have a definitive impact on the value of the end product. An example of a method for resolving such drawbacks is disclosed in JP (Kokai) 47-35103, wherein sodium

lauryl sulfate is employed as a foaming agent, but the effect of preserving the bubbles in a fine and dense state is virtually non-existent despite the foaming agent being effective in producing foam. On the other hand, the use of ammonium stearate, ammonium biphenate, or another higher aliphatic ammonium salt is disclosed in US Patent 3,804,700. Such compounds have an exceptional effect in preserving the bubbles in a fine state, but when the foam has been applied to a support and dried, numerous cracks will appear in the resulting coating layer, and the ammonium salt used after heat-induced gelation will migrate in large amounts to the surface of the layer, thereby considerably degrading the value of the resulting end product.

The present inventors conducted diligent investigations into resolving the drawbacks of resin compositions for mechanical foam coating as has been described in the foregoing, and perfected the present invention based on the discovery that extremely fine and dense foam could be obtained when a specific substance had been added to a resin composition, such a state could be preserved for long periods of time, no cracks would appear from drying, and the additives would not migrate to the surface even after the end product has been fabricated, thereby enabling a highly exceptional foam coating to be formed.

In other words, the present invention is a resin composition for mechanical foam coating comprising as principal components an aqueous medium, surfactant, and hydrophobic resin, with the resin composition characterized by being compounded with a higher aliphatic alcohol.

A detailed description of the present invention shall now be provided. The resin composition used as a base in the present invention encompasses all conventional resin compositions for mechanical foam coatings employed in relevant technical fields; e.g., acrylic resins, urethane resins, vinyl acetate resins, vinyl chloride resins, styrene resins, vinyl propionate resins, styrene-butadiene resins, acrylonitrile-butadiene resins, acrylonitrile-butadiene-styrene resins, polyisoprene, chloroprene, and natural rubber as well as other latexes, and can encompass a variety of additives as required; e.g., surfactants, gelling promoters, dyestuffs/pigments, fillers, antioxidants, stabilizers, viscosity adjusters, curing agents, and gelling agents.

The higher aliphatic primary alcohol that is used in the present invention and is a distinctive feature of this invention is a straight or branched chain synthetic or natural alcohol; e.g., octanol, decanol, lauryl alcohol, myristyl alcohol, cetyl alcohol, 14-methylhexadecanol,

stearyl alcohol, 16-methyloctadecanol, eicosanol, and 18-methylnonadecanol. Equally, synthetic alcohols having an odd number of carbons may also be used. It was discovered that primary alcohols having 9 to 20 carbons, and especially 14 to 20 carbons, were the most effective among these alcohols. The alcohols are preferably used in an amount of approximately 3 to 10 weight parts per 100 weight parts of resin in the latex.

The essential components of the resin composition for mechanical foam coating of the present invention are essentially the prior-art resin compositions for mechanical foam coating and the aforementioned higher aliphatic alcohols. However, it was discovered that particularly when acrylic or urethane resin compositions are used, the effect of the present invention could be dramatically enhanced by adding as an ancillary additive approximately 5 to 20 wt% of substantially unvulcanized (i.e., not yet subjected to a vulcanization step) natural (as well as modified) rubber latexes, aqueous dispersions of synthetic rubbers (latexes), or a mixture thereof to the acrylic or urethane resins (solid fraction), in addition to the aforementioned essential components. Examples of such natural rubber latexes include natural rubber latex and modified natural rubber latexes (e.g., natural rubber latexes that have been graft-polymerized with acrylic acid ester), and examples of synthetic rubber latexes include aqueous dispersions of the aforementioned varieties of synthetic rubbers and their modified synthetic rubbers. It was discovered that the effect of the present invention was significantly more pronounced when these substances were added.

The resin composition of the present invention is manufactured by using any conventional method to admix the higher aliphatic alcohol that characterizes the present invention, either alone or with the aforementioned rubber latexes, into the aforementioned conventionally known resin composition; however, it is normally advantageous to adjust the solid fraction to approximately 30 to 70 wt% and the viscosity to between approximately 5,000 and 20,000 cps in the steps described hereunder.

The resin composition of the present invention obtained as described in the foregoing is stirred mechanically by means of a common method; e.g., by means of an Oakes mixer as the air is blown thereinto to trap air in the material and to form a cream-like foam at a foaming rate of approximately 170 to 400%. Next, the foamed product is applied in a thickness of approximately

0.5 to 10 mm onto various optionally pretreated supports, heated and dried at a temperature of approximately 100 to 170°C, and formed into a heated gel to yield a foam layer. The bubbles in the cream-like foam obtained by mechanical means are very dense and fine, and these fine bubbles can be kept stable for extremely long periods of time, as compared to those obtained in the prior art. Adopting this approach makes it possible to substantially resolve problems related increased bubble sizes during subsequent steps; i.e., when the foam is applied to the support, dried, and caused to gel. With conventional methods, moreover, large bubbles form, and numerous cracks appear in the coated layer when the layer is dried, which largely degrades the value of the product. However, when the resin composition of the present invention is used, the bubbles essentially do not become large as the steps are performed, and therefore the occurrence of cracking in the coated layer is entirely eliminated, resulting in a foam coating layer that has exceptional hand, is extremely dense and highly flexible, and contains individual cells and communicating pores. Foam coating layers obtained by means of conventional methods generally exhibit poor physical characteristics at low temperatures, but the resin composition of the present invention was found to exhibit dramatically improved physical characteristics at low temperatures as well.

The resin composition for foam coating of the present invention may be applied to any support, and the foam coating later may be formed in various thicknesses. For example, the composition is advantageously utilized in the manufacture of synthetic leather, a variety of leather-like articles, cushioning sheets, decorative paper, decorative boards, wallpaper, and the like. In particular, using the resulting foam coating layer as a breathable cushioning middle layer and applying various coatings or surface treatments on the layer is preferred for the manufacture of a variety of synthetic leather, artificial leather, and other similar sheet-like products that resemble natural leather.

The present invention is described in detail below with reference to working examples. All references to "parts" or "%" in the description relate to weight.

Working Example 1

The three resin compositions I to III below were prepared according to conventional methods. The foam stabilizer of the present invention and a conventional foam stabilizer were

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added to these resin compositions to prepare the resin compositions for mechanical foam coating (A through C) in accordance with the present invention, and to prepare similar types of conventional resin compositions (a through j).

– Preparation of resin compositions (I to III)

Resin composition I

Polyacrylate ester emulsion (Rohm and Haas Co.; solid fraction: 50%):	100	parts
Crosslinking agent:	5	parts
Crosslinking catalyst:	0.5	parts
Thickener:	5	parts
Extender pigment (alumina):	10	parts

Resin composition II

Polyurethane emulsion (Bayer AG; solid fraction: 40%):	100	parts
Crosslinking agent:	5	parts
Crosslinking catalyst:	0.5	parts
Thickener:	5	parts
Extender pigment (alumina):	10	parts

Resin composition III

Polyacrylate ester emulsion (Rohm and Haas Co.; solid fraction: 50%):	50	parts
Polyurethane emulsion (Bayer AG; solid fraction: 40%):	50	parts
Crosslinking agent:	5	parts
Crosslinking catalyst:	0.5	parts
Thickener:	10	parts

– Preparation of resin compositions of the present invention (A to C)

Resin composition A: Mixture obtained by adding 5 parts of stearyl alcohol to 120.5 parts of resin composition I

Resin composition B: Mixture obtained by adding 5 parts of a synthetic primary aliphatic alcohol having 14 to 16 carbons and 10 parts of unvulcanized styrene-butadiene rubber latex (JSR Co., Ltd.; solid fraction: 60%) to 120.5 parts of resin composition II

Resin composition C: Mixture obtained by adding 5 parts of a synthetic primary aliphatic alcohol having 14 to 16 carbons and 10 parts of unvulcanized styrene-butadiene rubber latex (JSR Co., Ltd.; solid fraction: 60%) to 120.5 parts of resin composition III

– Preparation of conventional resin compositions (*a* to *f*; comparative resin composition)

Resin composition *a*: Mixture obtained by adding 5 parts of ammonium stearate to 120.5 parts of resin composition I

Resin composition *b*: Mixture obtained by adding 5 parts sodium of lauryl sulfate to 120.5 parts of resin composition I

Resin composition *c*: Mixture obtained by adding 5 parts of ammonium stearate to 120.5 parts of resin composition II

Resin composition *d*: Mixture obtained by adding 5 parts of sodium lauryl sulfate to 120.5 parts of resin composition II

Resin composition *e*: Mixture obtained by adding 5 parts of ammonium stearate to 120.5 parts of resin composition III

Resin composition *f*: Mixture obtained by adding 5 parts of sodium lauryl sulfate to 120.5 parts of resin composition III

Working Example 2

A formulation comprising 100 parts polyurethane elastomer solution (Rezamine ME; Dainichiseika Color & Chemicals Mfg. Co., Ltd.), 10 parts colorant (Seika Seven E color), and 20 parts solvent was applied to a release sheet and dried, resulting in 10 μ -thick films. The aforementioned resin compositions A to C and *a* to *f* were expanded to a foaming rate of 200% with the aid of a mechanical foaming mixer, and the resulting creamy foam was applied to the films in an amount that produced a thickness of 0.5 mm. A knitted base fabric was laminated under contact pressure on the coating layer at normal temperature, and the product was dried and caused to gel immediately thereafter for 10 min at 150°C, resulting in synthetic leather products. Evaluations were made of the bubbling state, product quality, and manner in which the foam stabilizer had migrated in the aforementioned steps. The results are shown in Table 1.

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Table 1

Resin composition	Bubbling state (note 1a)	Bubbling state (note 1b)	Product quality (note 2)	Migration of foam stabilizer (note 3)
A	Excellent	Excellent	Excellent	Excellent
B	Excellent	Excellent	Excellent	Excellent
C	Excellent	Excellent	Excellent	Excellent
a	Excellent	Good	Fair	Poor
b	Poor	Poor	Poor	Excellent
c	Excellent	Good	Fair	Poor
d	Poor	Poor	Poor	Excellent
e	Excellent	Good	Fair	Poor
f	Poor	Poor	Poor	Excellent

Note 1(a) A comparison was made between the bubbling states observed immediately after the products had expanded 200% and 10 minutes after the products had been left to stand, to examine the amount of aggregated large bubbles. "Excellent": no change at all; "Good": a small proportion of large bubbles; "Poor": significant proportion of large bubbles.

Note 1(b) The compositions were applied to Rezamine films immediately after the products had expanded 200%, and the amount of aggregated large bubbles was examined after the resulting articles had been left to stand for one minute. The levels of assessment were the same as those indicated in aforementioned Note 1(a).

Note 2 "Excellent": Surface film and foam layer were formed as integrated whole, and no cracks formed in the foam layer. The bubbles were extremely dense and fine.
 "Fair": Surface film and foam layer were formed as integrated whole, but the bubbles were fairly large, and numerous cracks appeared.
 "Poor": Pronounced formation of large bubbles, and poor surface state.

Note 3 The surface state of the products was observed after they had been immersed for 24 hrs in tap water at normal temperature, removed, and dried.
 "Excellent": No evidence of the foam stabilizer migrating to the surface.
 "Poor": Pronounced migration

Working Example 3

The aforementioned resin compositions A to C and *a* to *f* were each expanded 200% with a mechanical foaming mixer, applied to a base fabric (Moss 4A) in a thickness of approximately 0.4 to 0.5 mm with a knife coater, and then heated and dried to form a gel at 150°C for 10 min to yield original fabrics having foam layers that were approximately 0.2 to 0.3 mm thick. Synthetic leather products were obtained by applying the same film-forming compositions as those used in Working Example 2 onto these original fabrics at a rate of approximately 100 g/cm² using a knife coater, drying the resulting articles, then applying a polyamino acid resin topcoating agent at a rate of approximately 70 g/m², and drying the resulting articles. When the resin composition of the present invention was used in the manufacture of such products, a very good and uniformly fine bubbling state was obtained, large bubble aggregations did not form during the steps, the surfaces of the resulting products had the fine wrinkles seen in natural leather patterns, the layers of the product were completely integrated with each other, and no cracks appeared in the foam layer. Moreover, the surfaces were stable when washed with water or dry-cleaned, and there was no incidence of the foam stabilizer migrating to the surface. On the other hand, when resin compositions *a*, *c* and *e* were used, the resulting products were similar to those obtained with the resin composition of the present invention, but fairly large bubbles appeared in the foam layers, a high incidence of cracking occurred, the foam stabilizer migrated to the surface after the products were dried following a washing test, and the product value was significantly degraded. When resin compositions *b*, *d* and *f* were used, large bubbles formed when the foam was applied, the surface became very rough when the middle and surface layers were formed, and virtually no product value was retained.

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